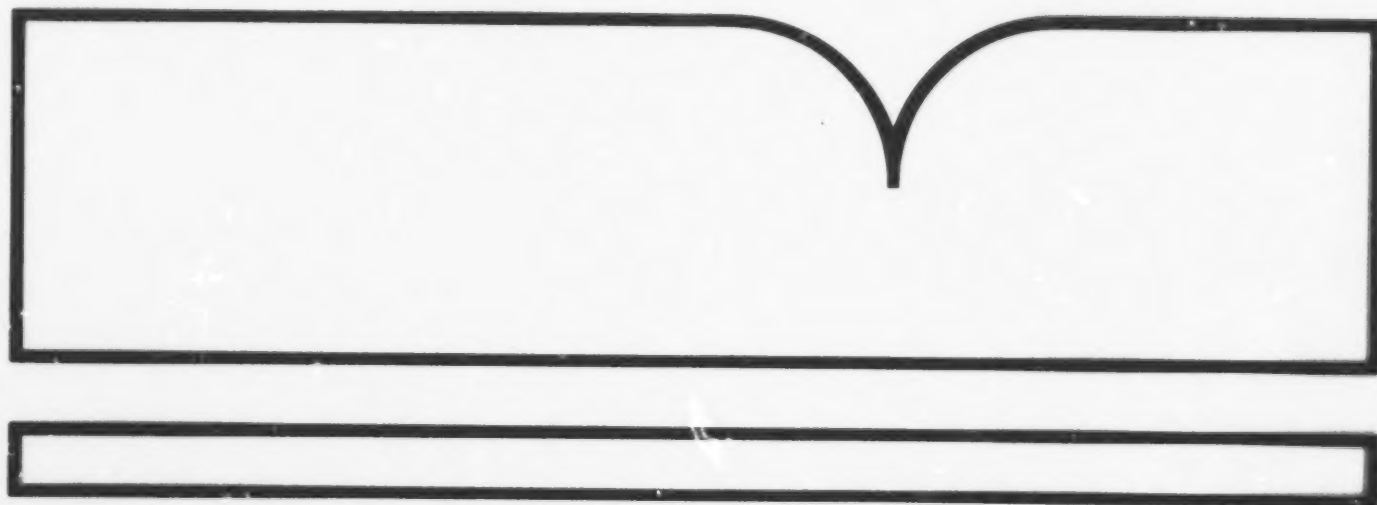


PB86-145794

High Reactivity Sorbents for SO₂ Control

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Jan 86



U.S. Department of Commerce
National Technical Information Service

NTIS

HIGH REACTIVITY SORBENTS FOR SO₂ CONTROL

by

Dennis C. Drehmel, David A. Kirchgessner,
and Samuel L. Rakes
U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)			
1. REPORT NO. EPA/600/D-86/009		3. RECIPIENT'S ACCESSION NO. D886 145794	
4. TITLE AND SUBTITLE High Reactivity Sorbents for SO ₂ Control		5. REPORT DATE January 1986	
7. AUTHOR(S) Dennis C. Drechsel, David A. Kirchgessner, and Samuel L. Rakes		6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS See Block 12		8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO. NA	
		13. TYPE OF REPORT AND PERIOD COVERED Published Paper; 12/85	
		14. SPONSORING AGENCY CODE EPA/600/13	
15. SUPPLEMENTARY NOTES AEERL project officer is David A. Kirchgessner, Mail Drop 4, 919/541-4021.			
16. ABSTRACT The paper discusses studies, relating to air pollution control from coal-fired utility boilers, that show that the primary variable affecting sorbent reactivity at high temperature or at low temperature with water droplets is surface area. For the development of high surface area during furnace injection, some limestones appear to be superior to others and can be selected accordingly. Even more striking are the differences in surface area development and sulfur capture between classes of commercially available sorbents. Dolomitic sorbents generally outperform their calcitic counterparts, and hydrates are clearly preferable to carbonates on the basis of SO ₂ capture. It has been shown further that sorbents can be modified in a number of ways to enhance their performance. Limestones can be precalcined to high surface areas and injected downstream from the burner to preserve their reactivity. Calcitic materials can be pressure hydrated to increase their reactivity over atmospheric hydrates, and hydration parameters can apparently be adjusted to increase reactivity even further. Finally, additives are available that promote SO ₂ capture in the full range of calcium-based sorbents, and iron has been identified as an effective promoter with minimal adverse effects when added to the water of hydration for pressure hydrated materials.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Sorbents	Pollution Control	13B 11G
Coal	Desulfurization	Stationary Sources	21D 07A
Combustion	Sulfur Oxides		21B 07B
Boilers	Limestone		13A 08G
Utilities	Iron		07D
Reactivity			
19. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES
		20. SECURITY CLASS (This page) Unclassified	22. PRICE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

BACKGROUND

EARLY DRY SORBENT USE FOR SO₂ CONTROL

During the late 1960's and early 1970's, the Environmental Protection Agency (EPA) and its predecessor organizations surveyed systems for air pollution control from coal-fired utility boilers. From this early work came developments such as limestone scrubbing for flue gas desulfurization (FGD) and low nitrogen oxide (NO_x) combustion technology.^(1,2) The forerunner of limestone scrubbing for FGD was dry limestone injection into the boiler firebox above the flame zone. EPA studied the use of dry sorbents for sulfur dioxide (SO₂) control from many aspects including: limestone characterization, limestone/SO₂ reaction kinetics, pilot-scale tests at both Peabody Coal Co. and Babcock & Wilcox, and full-scale tests at the Tennessee Valley Authority (TVA).

In the tests at Babcock & Wilcox,⁽³⁾ a down-fired pilot plant was designed to burn up to 9 kg/hr of coal. At 29.3 kWt and 15 percent excess air, sorbent injection ports were available at temperatures from 1480 to 815°C (2696 to 1499°F). In 415 tests, 129 different sorbents were studied while firing a variety of pulverized coals. Using up to double the calcium required, the degree of SO₂ control was typically between 21 and 34 percent,

although some sorbents (e.g., Michigan marl) achieved better than 40 percent SO₂ control. There was a large scatter in capture for both calcites and dolomites, but the averages of the two sorbent groups were essentially equal. Injection of extra sorbent did not improve control linearly but as the two-thirds power of the calcium/sulfur (Ca/S) ratio. Injection of sorbent with the coal gave poor SO₂ control (less than 8 percent). Fine grinding of the sorbent to surface areas greater than 1 m²/g improved reactivity, and hydrates and marls with surface areas greater than 9 m²/g were more reactive than other sorbents.

In the tests at Peabody Coal Company,⁽⁴⁾ the furnace was a chain grate stoker firing up to 200 kg/hr of coal. The fuel was 3.1 percent sulfur coal from western Kentucky. Of the sorbents tested, two were calcites, two were dolomites, and one was aragonite (a second crystalline form of calcium carbonate). Injection temperatures ranged from 980 to 1315°C (1796 to 2399°F), and SO₂ control ranged from 20 to 65 percent for the limestones. The aragonite was the best sorbent (followed by the calcites), and the dolomites were the least effective for SO₂ control. Sorbent mixed with the coal was not effective. Calcium oxide utilization improved dramatically from 6.3 percent for plus 100 mesh (149 μm) particles to 59.5 percent for minus 200 mesh (74 μm) particles.

In the tests at TVA,⁽⁵⁾ the site was Unit 10 of the Shawnee Plant firing coal at a nominal 150 MWe. Three sorbents were tested: aragonite and two calcites. One calcite was Michigan marl; the other was a fine-grained high-purity stone from Kentucky. Using twice the calcium required theoretically, the SO₂ control ranged from 17 to 20 percent, with the marl giving the best performance. The importance of time/temperature environment on SO₂ control was demonstrated by reducing the boiler to half load. At half load the sorbent residence time at 926 to 1204°C (1989 to 2199°F) was increased, resulting in SO₂ control as high as 36 percent.

DRY SORBENTS USED WITH LOW NO_x BURNERS

In the late 1970's, developments at Energy and Environmental Research Corporation (EERC) renewed interest in dry sorbent injection. EERC conducted a short series of experiments with sulfur capture using a low NO_x distributed mixing burner (DMB) which had recently been developed.⁽⁶⁾ The advantage of this burner is the delayed mixing of fuel and air which lowers temperature and provides reducing gases to convert fuel nitrogen to N₂. The tests fired coal at a rate producing 3.5 Mwt. Fuels used were a 0.7 percent sulfur Utah coal and a 3.8 percent sulfur Kentucky coal. Sorbents used included limestone and nahcolite which were mixed

with coal for these tests. The SO₂ control achieved with limestone was 53 percent with low sulfur coal and 50 percent with high sulfur coal when the sorbent injection rate was at the stoichiometric requirement. At two and three times stoichiometric, the SO₂ control rose to 73 and 88 percent, respectively, with the low sulfur coal. In discussing these results, EERC noted the following differences using the DMB which might account for high levels of SO₂ control:

- 1) The low NO_x DMB provides an optimum time/temperature profile. Peak temperatures in the DMB would be lower, giving less opportunity for the limestone to lose reactivity to physical changes. Longer residence times at lower temperatures provide more time for the sulfation reaction.
- 2) Peak flame temperatures occur under fuel-rich conditions where limestone could react with reduced sulfur species. Sulfidation reactions are faster than sulfation reactions, and the product calcium sulfide would be more stable than calcium sulfate.
- 3) Effective sorbent distribution was provided by mixing the sorbent with the coal.

Because of the initial good SO₂ capture data, the possibility of simultaneous NO_x and SO₂ reduction became the focus of on-going EERC research. At that time low NO_x prototype burners were being tested in a 23 MWT coal-fired furnace called the large watertube simulator (LWS). The prototype burners were of Steinmuller and EPA design, the latter referred to as "the prototype burner" because it was to be used for a demonstration of low NO_x burners in the U.S. The SO₂ capture data ranged from 30 to 50 percent at a Ca/S ratio of 2 for these early LWS tests.^(7,8) Sulfur capture was a function of both the sulfur concentration in the coal and the type of burner. Because sulfur capture was lower in these tests, it was decided to build a furnace which would give flue gas cooling conditions similar to a boiler and to perform extensive parametric tests.

Early results from the boiler simulator furnace (BSF) showed a wide range of possible SO₂ captures depending on furnace firing rate, heat extraction rate, and limestone injection conditions.^(7,8) Thus the BSF results were shown to be in agreement with those from early limestone injection tests noted above. However, as BSF testing continued, different insights into the limestone/SO₂ reaction were formulated. While thermal deactivation of limestone had been a major concern at Shawnee, a different deactivation - chemical -

was proposed⁽⁹⁾ and then confirmed⁽¹⁰⁾ from the BSF tests. Another insight was that conditions giving long residence times with reduced sulfur species ("external staging"⁽⁹⁾) did not enhance overall sulfur capture. In a study by Exxon,⁽¹¹⁾ poor capture of H₂S by limestone was also observed at 1065°C (1949°F) and 1.5 seconds residence time. Thus, in spite of potential good kinetics for the limestone/H₂S reaction, it does not appear that an advantage of limestone injection with low NO_x burners is the presence of reduced sulfur species giving higher capture.

While the above new insights are generally negative, there were two positive results: (1) there is a spectacular difference in the performance of different sorbents; and (2) chemical activation and deactivation are both possible (i.e., there are chemicals which, when added to a sorbent, promote the effectiveness of the sorbent for sulfur capture). Both of these positive insights resulted in studies to define the differences between sorbents and the role of promoters to produce highly reactive sorbents. This paper summarizes the results of those studies as well as results from earlier studies.

EXPERIMENTAL

FURNACE DESCRIPTION

The EPA small coal-fired furnace (SCF) at Research Triangle Park (RTP), NC, was used for dry sorbent testing at high temperature. The unit is a 155 mm (6 in.) internal diameter down-fired unit. Three burner configurations may be used: axial-fired, radial-fired, and a premix configuration with provision for tangential or swirl air. Each configuration may employ the distributed-mixing burner (DMB) concept. In the premixed burner, this is accomplished by mixing less than the total air in the burner and adding the remainder of the air after the burner.

The firing rate of the furnace is adjustable, with a nominal rating of 100,000 Btu/hr (29.6 kWt) or about 3.2 kg coal/hr. Stable operation at a rate of about 1.4 kg coal/hr (42,000 to 50,000 Btu/hr) is normal for testing. The unit may be fired on natural gas, propane, or coal.

The unit is of conventional construction with rolled steel rings 762 mm (30 in.) in diameter and 300 mm (1 ft), 450 mm (1.5 ft), or 600 mm (2 ft) high. The steel rings are insulated

by four courses of refractory: beginning on the outside with a good insulating, low strength castable block mix refractory; progressing inward with castable insulation; following with Castolite 30;* and ending on the inside with a high strength, erosion resistant "hard face" refractory such as Green Cast 97. After casting the refractory into the steel rings, the rings are "stacked" using a gasket made of Kaowool or similar material on the outer periphery.

Nine thermocouples, embedded in the refractory approximately 12 mm (1/2 in.) from the combustion gas central passage, are spaced over the furnace section. Nine ports, approximately opposite the thermocouple locations, are usable for either sampling or injection. The final furnace section contains cooling water coils to quench any reactions before the sample is extracted for the continuous monitors.

Solid fuel, such as coal, is metered from a K-Tron™ loss-in-weight feeder. A similar feeder, but suited to delivery of a smaller amount, meters the sorbent, such as limestone or lime. The sorbent material is aspirated and transported by air and injected into the furnace through a water-cooled probe.

(*) Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. EPA.

Operating conditions and emissions are monitored using the following instruments:

Digistrip III™ Data Logger

Continuous Monitors:

CO	Beckman Model 864 Infrared
CO ₂	Beckman Model 864 Infrared
O ₂	Beckman Model 755
SO ₂	Anacon Model 207 U.V.
NO, NO ₂ , NO _x	Thermoelectron Model 10AR
HC	Beckman Model 402

Thermocouples, both B&K types, embedded or sealed in the refractory.

In addition, gas temperatures are measured using suction pyrometry with stabilized run conditions equal to those in the tests. No significant temperature profile difference was found between gas firing and coal firing at equal heat input rates, based on fuel heating value and excess air conditions.

SORBENT DESCRIPTION FOR HIGH TEMPERATURE TESTING

The Vicron limestone is designated as 45-3, in reference to the nominal particle size range of the cut or fraction used. When

tested, 99.2 percent passed through a 60 mesh (250 mm) sieve.

The material referred to as dihydrate is $\text{MgO} \cdot \text{CaO}$ pressure-hydrated to $\text{Mg}(\text{OH})_2 \cdot \text{Ca}(\text{OH})_2$ from the Henderson, Nevada, plant of the Genstar Corporation. It is a commercial product. Wet sieve testing gave 90.0 percent passing through a 150 mesh (106 mm) screen and 79.0 percent passing through a 325 mesh (45 mm) screen.

The calcium hydroxide is a technical grade laboratory supply item, Fisher No. C-88. No special storage precautions, other than closing the bag after removing the test charge, were used. The sieve test showed 99.5 percent passing through a 60 mesh (250 mm) sieve.

SORBENT DESCRIPTION FOR LOW TEMPERATURE TESTING

Twelve basic carbonate rock types were selected for the low temperature study. The first nine types correspond identically to the nine types of Harvey.⁽¹²⁾ Types 10, 11, and 12 correspond to Georgia marble (No. 1336), Michigan marl (No. 2129), and Kansas chalk (No. 2081), respectively. One additional limestone was investigated for effects of calcination temperature on dissolution rate: this fine grained oolitic stone (sometimes referenced as No. 2061) was calcined at several temperatures from 927 to 1760°C

(1700 to 3200°F). The physical properties and reactivity of these calcines have been discussed.⁽¹³⁾ Complete petrographic and chemical analysis of all of the carbonate rocks used in this study has been given by Harvey and is summarized in Table 1. Calcines of these carbonate rocks were prepared by 2 hour batch heating in an electric furnace.

RESULTS

In addition to the proposed use of limestone during combustion, many current and proposed post-combustion control processes use the calcined limestone resulting from furnace injection. While the properties of limestones vary greatly, this variability would not necessarily affect performance for all processes. However, in the two cases where limestone is used dry at high temperatures or at low temperatures with water drops, limestone properties are important as shown in the following results.

HIGH TEMPERATURE

The performance of different sorbents at high temperature can be studied either from the variables under direct control (e.g., sorbent type, pretreatment, particle size, and activation associated

TABLE I. CHEMICAL ANALYSIS^a AND PETROGRAPHIC CHARACTERISTICS

Sample Type No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	CO ₂	Mineralogy ^b	Petrographic Type
1	N11	N11	N11	N11	55.3	43.95	Calcite	Iceland spar rhombs
2	N11	0.01	0.19	N11	55.5	43.35	Calcite	Spar
3	N11	N11	0.20	1.86	53.4	43.75	Calcite (dolomite)	Coarse limestone
4	1.53	0.01	0.31	0.00	54.8	43.35	Calcite (quartz)	Fine limestone
5	0.03	0.02	0.34	21.40	30.30	47.30	Dolomite	Reef dolomite
6	11.8	1.77	0.13	17.4	26.5	40.27	Dolomite (quartz, clay)	Nonreef (impure) dolomite
7	0.47	0.08	N11	44.2	2.93	50.96	Magnesite	Fine magnesite
8	0.19	0.27	N11	N11	55.2	42.10	Aragonite	Oolitic sand
9	5.88	0.69	2.82	15.33	30.82	40.68	Dolomite (calcite, quartz)	Calcitic dolomite
10	0.85	0.20	0.15	1.4	53.7	43.4	Calcite (tremo- lite)	Marble
11	3.63	0.95	N11	N11	46.6	37.18	Calcite (quartz, clay)	Bog marl
12	2.48	1.09	0.15	1.41	51.4	39.44	Calcite	Chalk

^a Each numerical value is a percentage by weight^b Minor mineral constituents are given in parentheses

with injection location) or from the variables under indirect control (e.g., surface area and pore size distribution). Considering direct variables first, Figure 1 contains typical information about sorbent type and sorbent activation associated with injection location. These data are from the small coal-fired furnace (SCF) described above. Three types of sorbents are shown: limestone, calcitic hydrate, and dolomitic hydroxide hydrated under pressure to hydrate both the calcium and magnesium oxides (hence, the designation of dihydrate). Two injection locations were used; one at the burner and the second at a lower temperature. In all cases, the lower temperature injection was better. However, the change in temperature affects the three sorbent types differently. The limestone loses only a small part of its reactivity at the higher temperatures at the burner, while the other two lose reactivity dramatically. The loss of reactivity of the calcitic hydrate is sufficient to change the general ranking of sorbent types. In general, the dolomitic dihydrate is more reactive than the calcitic hydrate which is better than limestone. However, with burner injection, limestone is more reactive than calcitic hydrate. Note that changing to gas as a fuel does not change the sorbent rankings for the same injection location.

The pretreatment option is illustrated in Figure 2 which also shows data from the SCF. In this case, Vicron, which is a high

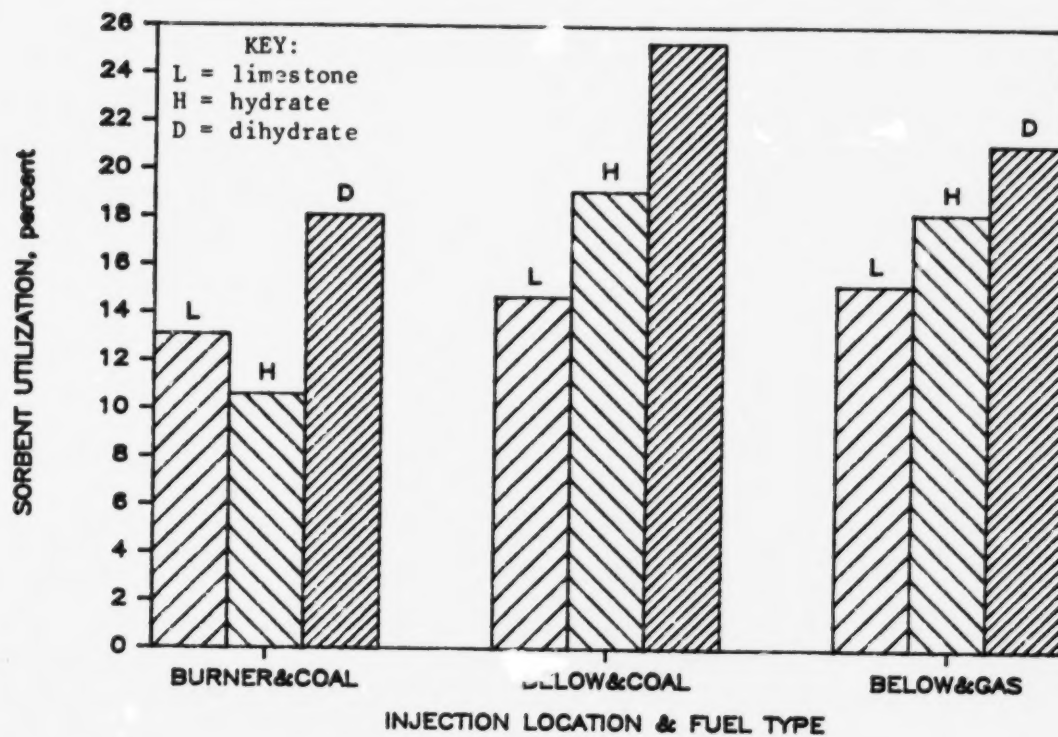


Figure 1. Three types of sorbents.

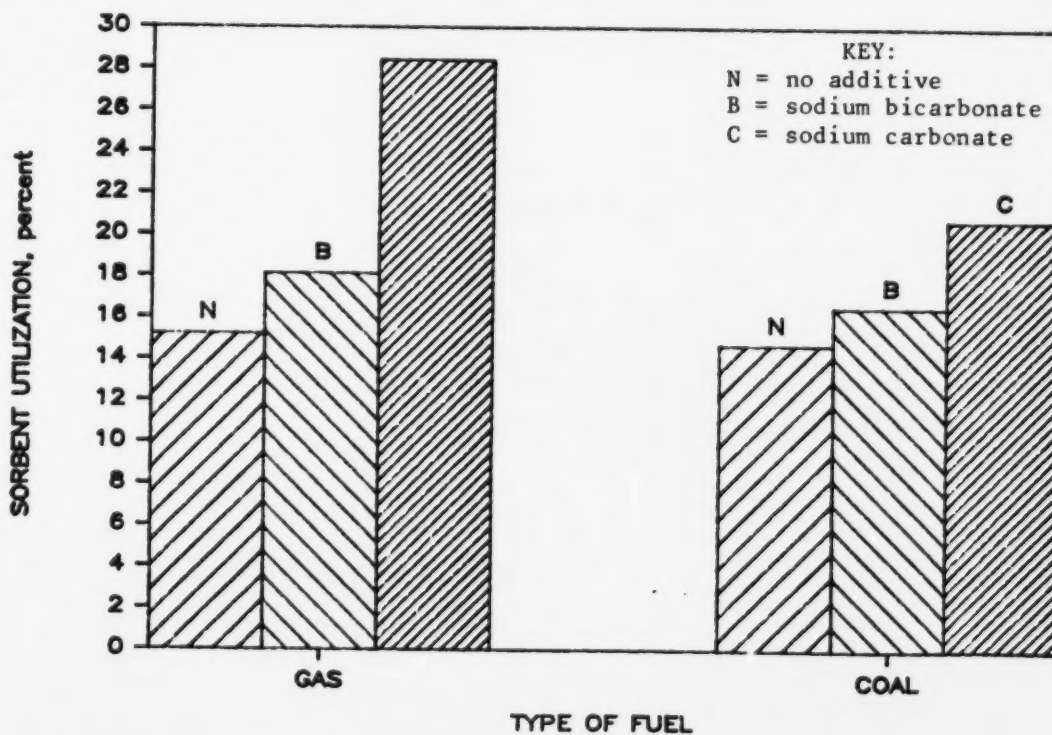


Figure 2. Promotion by sodium compounds.

calcium limestone, has been treated with 5 percent (by weight) sodium compounds--either sodium carbonate or sodium bicarbonate. The best improvement in SO_2 capture is for sodium carbonate addition under gas firing conditions. Switching to coal firing reduces the improvement. Even less improvement is seen with the bicarbonate. Because the pretreatment was on a total weight basis, the bicarbonate addition provides approximately half of the sodium which the carbonate addition provides. Other experiments have shown the improvement to be approximately linear with sodium addition. As with carbonate, switching from gas to coal firing lowers the improvement seen with bicarbonate.

Considering indirectly controlled variables, the most informative is surface area. The direct relationship between SO_2 capture and surface area for two different furnace temperature profiles (quench rates) is illustrated in Figure 3. The important observation is that the differences between sorbent types (limestone, calcitic hydrate, and dolomite) can be largely accounted for by surface area. With regard to quench rate, it is a measure of the steepness of the furnace temperature profile and inverse to the time the sorbent spends at temperatures favorable for reaction. The figure shows that higher quench rates give lower SO_2 capture; i.e., shorter residence times give lower SO_2 capture.

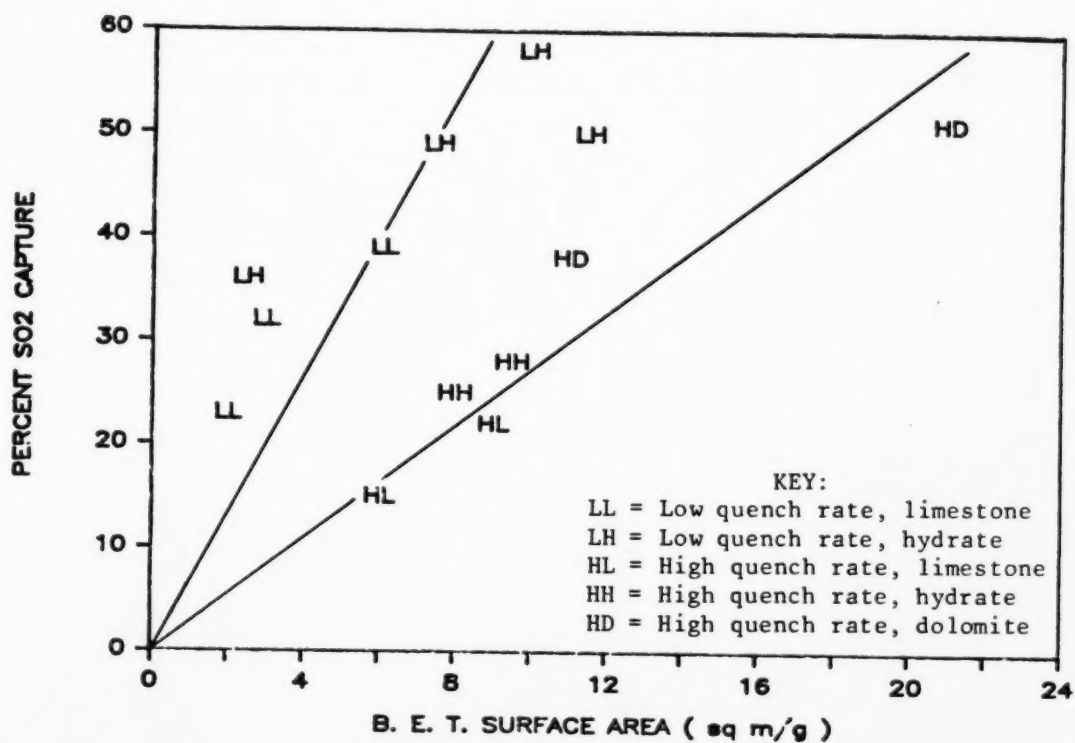


Figure 3. Effect of surface area.

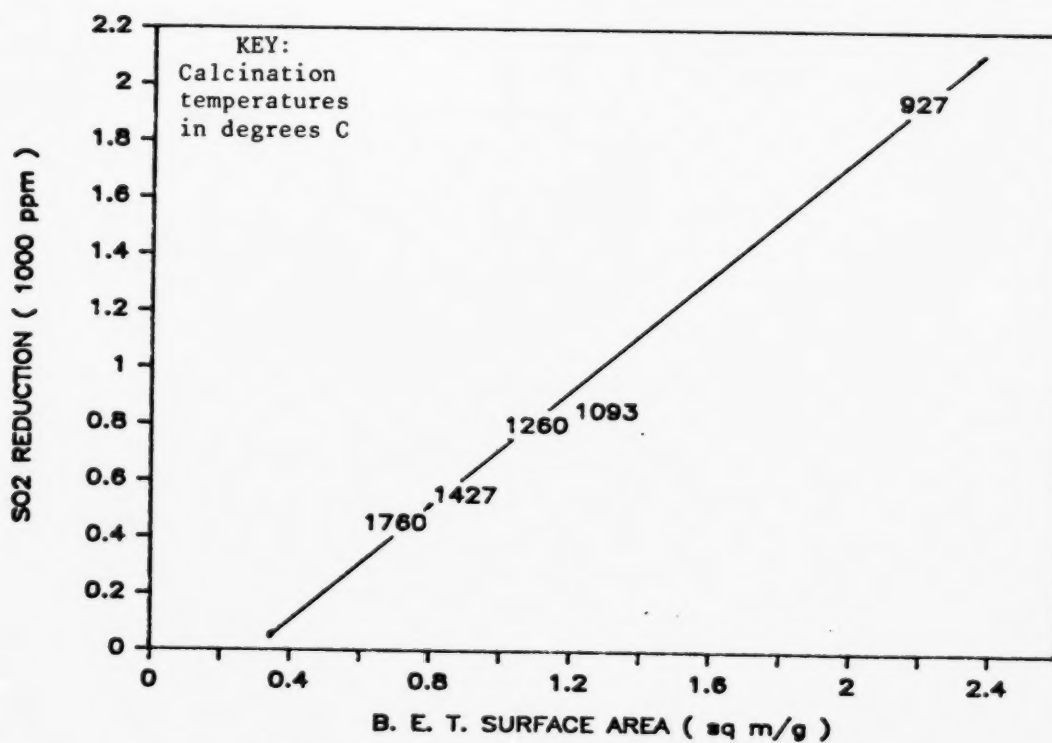


Figure 4. Effect of calcination temperature.

While it had been established that surface area was the predominant parameter controlling sorbent reactivity, it was not clear what relationship sorbent particle size had to reactivity or how surface area and particle size were interrelated. Recent experiments have revealed that particle size acts as a limiting factor because of pore diffusion. If the particle is very small (less than 1 μm), it has no effect on sorbent reactivity, and surface area controls the sorbent reactivity. As the particle size increases for a given mass, less particle surface area is readily available and SO_2 must diffuse through pores to reach the surface area. Hence, when the particle is very large, the pore diffusion becomes the limiting factor, and surface area has a small effect. Of course, with very large particles the sorbent reactivity is also very small so that large particles are not of interest. The particle size should be made as small as economically possible to avoid the pore diffusion limitation and utilize the full reactivity of the surface area generated by the chosen sorbent.

LOW TEMPERATURE WITH WATER DROPS

The performance of different sorbents at low temperature with water drops can be studied from the perspective of dissolution rate. Other studies have shown that calcium-based sorbent reactivity is

low without water drops or closely approaching the dew point. Thus, the alkali must get into the aqueous phase to be effective. If sorbent and water to make droplets are not premixed, the time for dissolution is limited to the residence time of water drops in the flue gas or less than 10 seconds. Hence, dissolution rate will be important, and relative sorbent performance can be predicted by dissolution rate.

Two methods were used to study dissolution rate. The first was a direct procedure using the Eckhard coarse grain acid titration test. In this method 1 g of sized sample is slurried in 200 ml of distilled water and titrated at minute intervals with sulfurous acid to pH 7. From these data, a curve of cumulative acid consumed versus time is drawn. In order to have a numerical estimate of the dissolution rate during the initial portion of the curve, the predicted consumption of acid at 1 minute from the smooth curve was used to compute the equivalents of acid consumed per time and volume.

The second method was an indirect procedure which monitored the impact of alkali addition to water saturated with flue gas bubbling through the water. This should simulate the impaction of alkali particles on water drops in a flue gas environment. The apparatus consisted of 1-liter temperature regulated water/flue gas

contactor and a small side vessel (approximately 250 ml); total volume of the system was 1500 ml. The liquor was continuously circulated between the scrubber and side vessel at 3 liters/minute. Flue gas with 3000 ppm SO_2 was bubbled through the liquid at $0.28 \text{ N m}^3/\text{h}$. After an initial period of bubbling flue gas through the water, the effluent SO_2 concentration would stabilize at a value slightly below the SO_2 concentration in the flue gas. At this time approximately 0.5 g of limestone or 0.25 g of lime (weight necessary for 0.01 alkaline equivalents) was added to the side vessel, and the change in effluent SO_2 concentration was recorded. The reduction in SO_2 would rapidly reach a peak and gradually fall to zero. The peak reduction in SO_2 concentration due to the addition of 0.01 alkaline equivalents of sized samples was reported. The peak SO_2 reduction is thus a measure of the rapidity of alkali dissolution.

Results of the direct measurement of dissolution rates for calcined carbonate rocks from an acid titration are given in Table 2. These data were obtained at 21°C (70°F) for 1 g of 42 to 65 mesh (355 to 212 μm) stone calcined at 1093°C (2000°F). The only obvious general observation is that some of the coarse-grained calcites and some of the dolomites have low dissolution rates and that aragonite (the other crystal form of CaCO_3) had the highest dissolution rate.

TABLE 2. ESTIMATED DISSOLUTION RATES OF
CALCINED CARBONATE ROCKS^a

Type	Description	Dissolution Rate (meg/min./g)
1	Iceland spar	20
2	Calcite spar	9
3	Coarse grained limestone	10
4	Fine grained limestone	12
5	Reef dolomite	13
6	Non reef dolomite	6
7	Magnesite	4
8	Aragonite	25
9	Calcitic dolomite	6
10	Marble	7
11	Marl	13
12	Chalk	15

^a Calcined at 1093°C (2000°F), 42 to 65 mesh (355 to 212 μ m)

Results of the indirect measurement of dissolution rate via peak SO_2 reduction were compared to B.E.T. surface area and pore volume using a mercury porosimeter. Correlation coefficients between dissolution rate or peak SO_2 reduction and physical properties were computed. Data from uncalcined carbonate rocks yielded only insignificant correlation coefficients. For calcined stone several correlations were observed. With calcination temperature as the parameter (see Figure 4), the correlation coefficient for peak SO_2 reduction versus surface area is 0.99 and versus total pore volume is 0.98. This agrees with the previous study(13) that found strong correlations between surface area or pore volume and several measures of reactivity.

With carbonate rock type as the parameter, peak SO_2 reduction also shows a dependence on both surface area and pore volume. For 150 to 170 mesh (106 to 90 μm) stones calcined at 1093°C (2000°F) for 2 hours, variance in surface area predicts the variance in relative dissolution rate of the high calcium oxide stones except for marl and chalk (see Figure 5). On the other hand, pore volume appears to account for the high relative dissolution rate of marl and chalk while the data for calcites remains somewhat scattered in Figure 6.

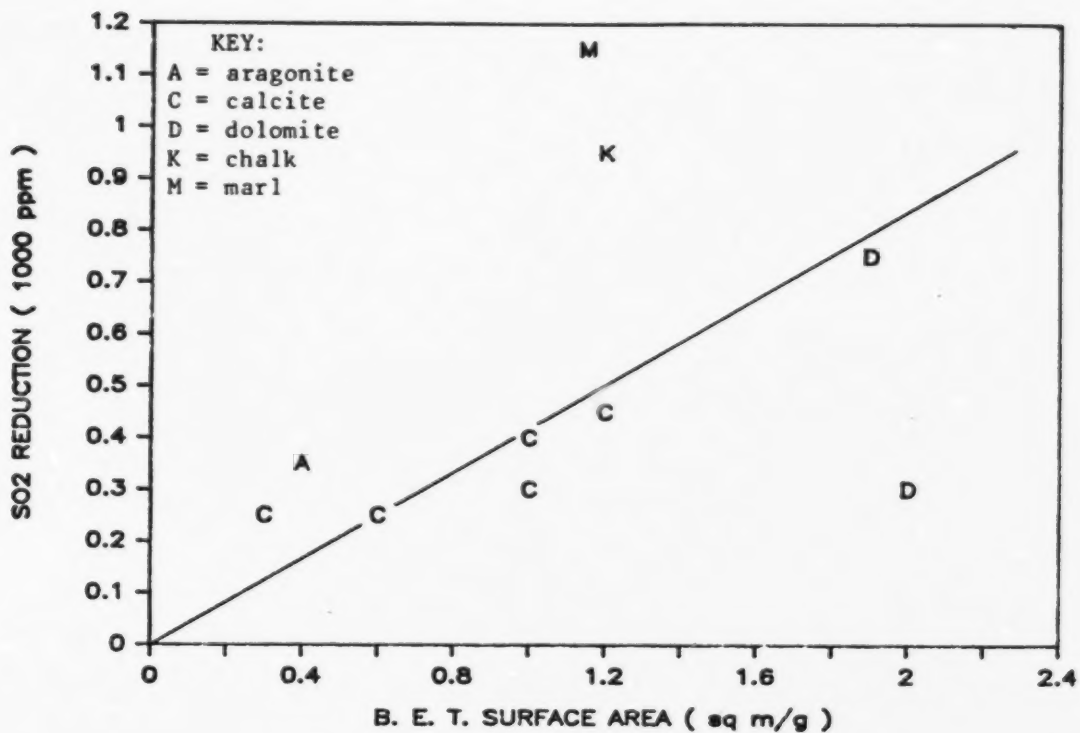


Figure 5. Types compared by surface area.

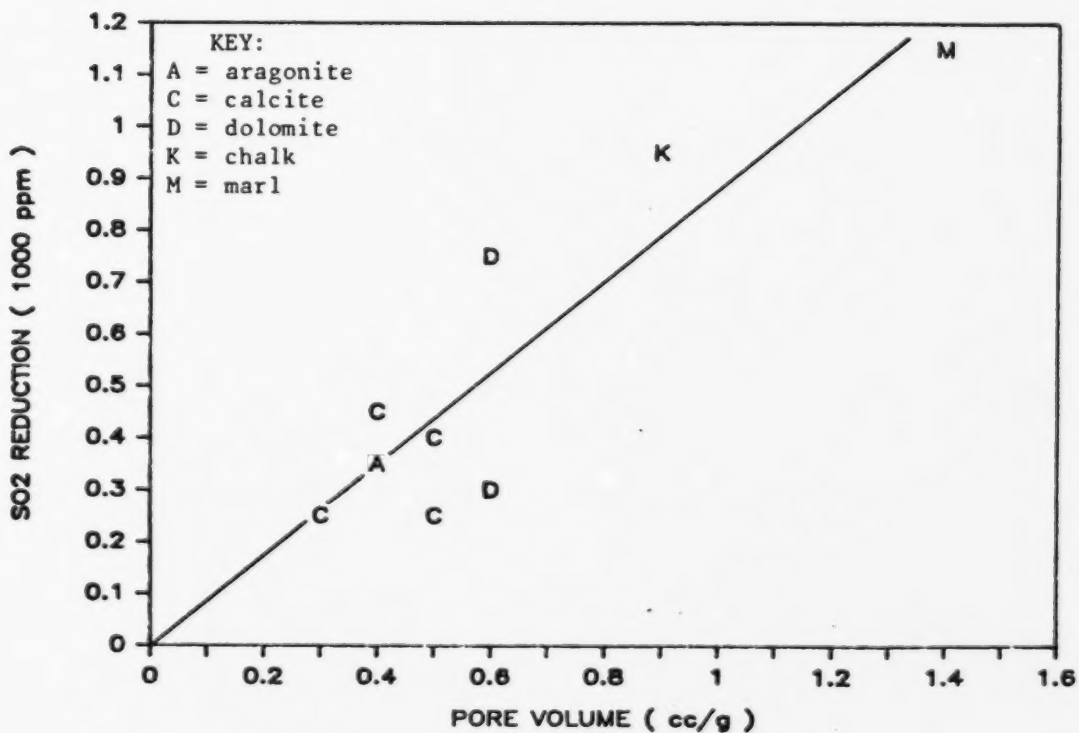


Figure 6. Types compared by pore volume.

SORBENT OPTIMIZATION

Having demonstrated experimentally that high surface area and the addition of promoters enhance the ability of sorbents to capture sulfur, a method of using these properties to maximize sulfur capture in the boiler system is needed. One option is to maximize the surface area developed in the furnace through the proper selection of materials to be injected. Another option is to produce high surface area sorbents outside the furnace and inject the resulting precalcines at the optimal position in the high temperature sulfation temperature window or at low temperature with co-injection of water drops. A third possibility is to alter the parameters under which commercial sorbents are currently produced so that they achieve higher surface areas when injected into the furnace. The fourth potential means of achieving high SO_2 capture is to add promoters to the sorbents prior to injection.

SORBENT SELECTION

Several lines of evidence indicate that surface areas, and the resulting SO_2 captures, vary with the choice of sorbent injected into a furnace. A wide range of surface areas and sulfur captures have been achieved with different commercially available materials.

Investigations at EPA's Research Triangle Park (RTP), NC, laboratory have shown that different commercially available limestones and dolomites calcined under identical conditions achieve significantly different maximum surface areas. Figure 7 shows previously reported results⁽¹⁴⁾ of 10 materials screened to a top size of 325 mesh (45 μm) and calcined at 850°C (1562°F) for 30 minutes in a still air environment. The superior performance of dolomites as a group is evident and has been widely observed. It was surprising, however, to note that the maximum surface areas developed by limestones varied by as much as a factor of three from one another. It is assumed that these same stones would also exhibit a range of surface areas and sulfur captures when injected into a furnace environment. Separate studies at the University of Utah by Newton et al.⁽¹⁵⁾ and Harrison et al.⁽¹⁶⁾ have verified the correlation between surface areas produced in these types of calcination studies and SO₂ capture in an experimental furnace.

Experimental evidence also exists to demonstrate that different classes of commercially available calcium-based sorbents vary widely with respect to surface area development and sulfur capture during furnace injection. Table 3 summarizes test results produced in three separate pilot-scale research efforts: Overmoe et al.,⁽¹⁷⁾ Beittel et al.,⁽¹⁸⁾ and Bortz and Flament.⁽¹⁹⁾ The data in this table show a clear and relatively consistent rela-

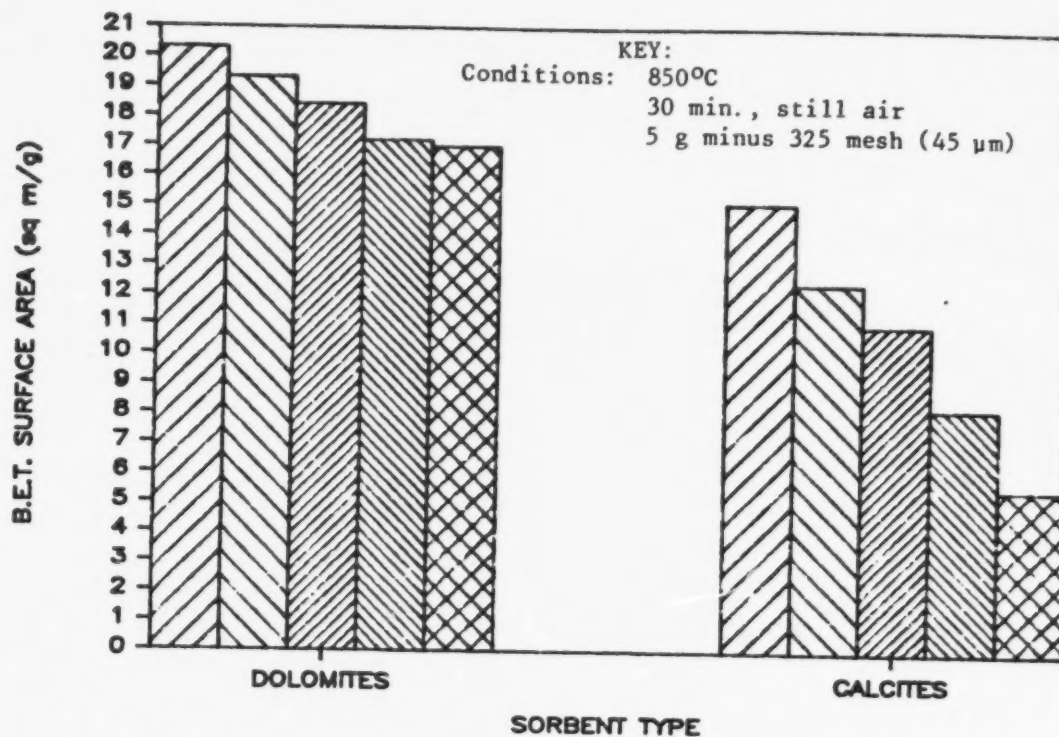


Figure 7. Batch calcinations.

TABLE 3. PERCENT SO₂ CAPTURES ACHIEVED WITH DIFFERENT CLASSES OF CALCIUM-BASED SORBENTS

Reference	Approximate Injection Temperature, °C	Percent SO ₂ Capture at Ca/S = 2			
		Limestone	Calcium Hydroxide	Dolomite	Pressure Hydrated Dolomite
Overmoe et al.(17)	1230	30	42-48	57	74
Beittle et al.(18)	1200	40	50-60	55	70-80
Bortz & Flament(19)	1200	30-40	65-80	--	--

tionship between the classes of sorbents: dolomitic sorbents are always better than calcitic sorbents and hydroxides are better than carbonates. Slaughter et al.(20) at the University of Utah demonstrated the same order of reactivities in a smaller isothermal reactor. Both Beittle's and Slaughter's investigations experimentally demonstrated the correlation between surface area and SO_2 capture.

Briefly then, experimental evidence compiled thus far strongly implies that limestones vary from one to another in their reactivity with SO_2 after calcination. Still more compelling is the evidence which suggests that much greater SO_2 captures can be achieved by substituting a hydrated sorbent for a carbonate. Although dolomitic carbonates consistently appear to outperform calcitic carbonates and dolomitic hydrates are superior to calcitic hydrates on an equivalent calcium basis, Newton et al.(15) have concluded that (on an equivalent mass basis) dolomitic materials probably offer no significant advantage over calcitic materials. Calcium hydroxide, therefore, appears to be the sorbent of choice among those currently commercially available unless only dolomitic materials are practically available in a given area.

MODIFICATION BY PRECALCINATION

A second method of making a high surface area sorbent available to the sulfation temperature window is to precalcine the material under optimal conditions outside the boiler and inject the material at approximately 1230°C (2246°F). A project at EPA's RTP laboratory developed a method of producing high surface area precalcines from carbonate materials using technology amenable to scale-up. The small, quartz fluidized-bed calcination unit shown in Figure 8 was designed and constructed for operation in a muffle furnace. Eighteen commercially available limestones were crushed, screened to minus 28 mesh (600 μm), and calcined in the reactor at temperatures ranging from 700 to 850°C (1292 to 1562°F) for 30 minutes with an air flow of 7 liters/min. Figure 9 is a histogram of the distribution of maximum surface areas achieved under these conditions. Surface areas ranging from 24 to 59 m^2/g were formed in the materials with modal values in the 35 to 40 m^2/g range. This represents a substantial increase over commercial limes which develop surface areas of around 1 m^2/g . While production of these materials at laboratory-scale provides an initial proof-of-concept for the technique, the effects of varying particle size, air flow, and composition of the fluidizing medium need to be studied. Economic feasibility also remains to be demonstrated.

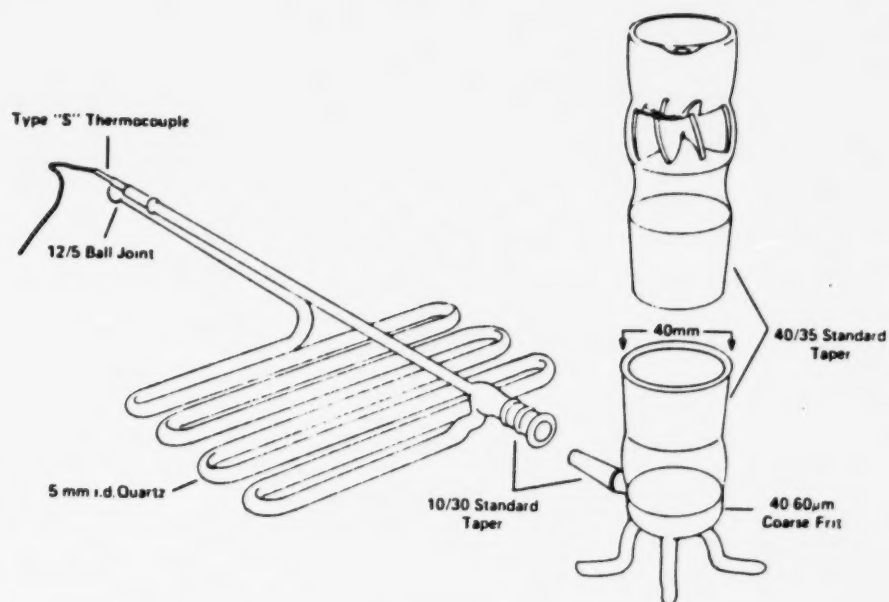


Figure 8. Fused quartz fluidized-bed calcination unit.

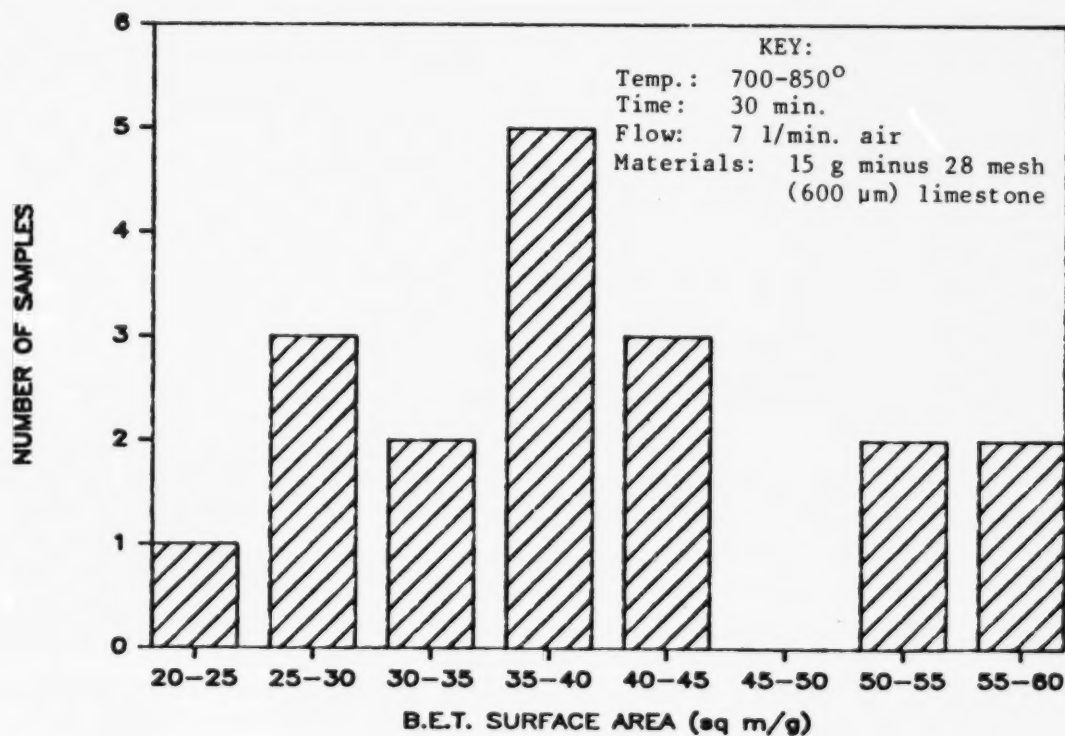


Figure 9. Fluidized-bed calcination.

MODIFICATION OF HYDRATION PARAMETERS

Once it has been demonstrated that different classes of commercial sorbents vary in their reactivity with SO_2 , the question arises of which production parameters are most important in optimizing their reactivity. Because of the impressive results seen thus far with hydrated materials, attention has focused on them. Since pressure hydrated dolomites consistently outperform other sorbents in SO_2 capture, it is necessary to determine whether the enhanced reactivity is caused by the presence of dolomite or the process of pressure hydration. To make this determination, EERC has pressure hydrated a number of calcined limestones and compared their reactivity with those of the same limestones atmospherically hydrated. Pressure hydrated limestones produced under controlled conditions appear to be superior to atmospheric hydrates in capturing SO_2 . The results of boiler simulator furnace (BSF) testing shown in Figure 10 demonstrate the superiority of one pressure hydrate over a range of injection temperatures.

Both atmospheric and pressure hydrates are known to vary in their reactivity with SO_2 . Work performed by EERC suggests that the variability in reactivity of pressure hydrates correlates with: 1) particle size of the parent quicklime; 2) water content

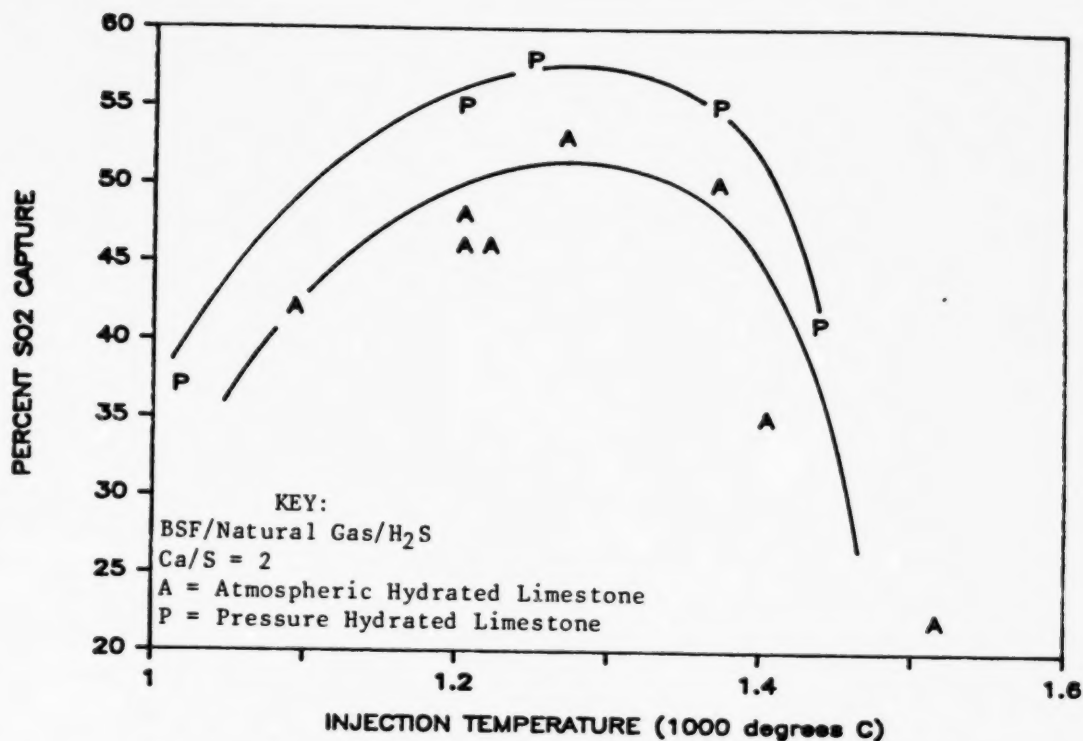


Figure 10. The effect of pressure hydration on SO₂ capture by calcium hydroxide.

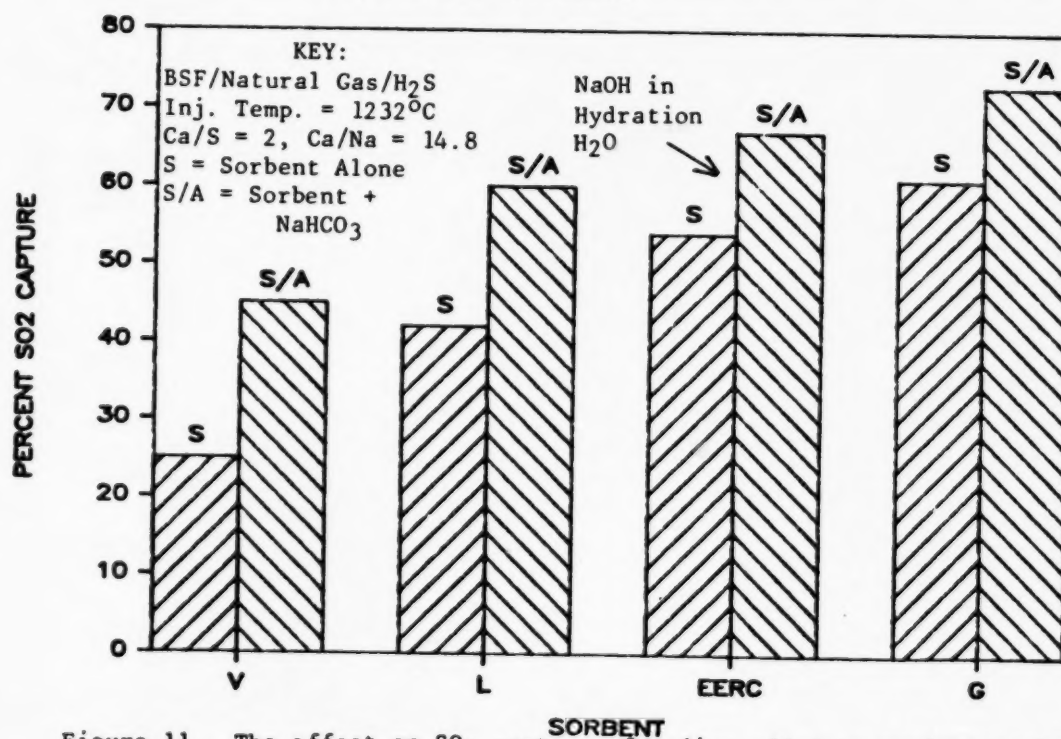


Figure 11. The effect on SO₂ capture of sodium added to various sorbents (V = limestone, L = atmospheric hydrated limestone, EERC = pressure hydrated limestone, G = pressure hydrated dolomite).

of the quicklime prior to hydration; 3) the rate of water addition; and 4) the manner of discharge from the hydrator. Carefully designed and controlled parametric studies at EPA and at Southern Research Institute will be employed to determine the relative importance of various process parameters for both atmospheric and pressure hydrates.

MODIFICATION WITH PROMOTERS

The effectiveness of sodium compounds in promoting the reactivity of sorbents with SO_2 was pointed out earlier in this paper. Research efforts during the past 2 years have been focused on various compounds to identify additives which are effective promoters, while being environmentally, economically, and technically acceptable. Early survey work by Borgwardt et al.⁽²¹⁾ included over 30 different compounds. The effects of various additives ranged from increasing to decreasing reactivity by a factor of 5.

Subsequent work by EERC has focused mainly on sodium- and chromium-based promoters to establish the mechanisms by which they work, and their optimal mixing with sorbents. Chromium, while environmentally and economically unacceptable in practical applications, has proven instructive in the mechanistic studies since it

is an effective promoter that differs greatly from sodium in its properties. Figures 11 and 12 show the enhanced reactivity produced in various sorbents by sodium and chromium, respectively. Testing was conducted in the BSF with natural gas and coal as the fuels. Figure 11 shows that intimate physical mixing of NaHCO_3 with limestone, atmospheric hydrated limestone, and pressure hydrated dolomite nearly doubles SO_2 capture in some cases. Adding NaOH to pressure hydrated limestone in the water of hydration increases SO_2 capture by about 23 percent. Figure 12 shows that physically mixing Cr_2O_3 with limestone, atmospheric hydrated limestone, and pressure hydrated limestone increases capture by up to 62 percent. It also shows that adding CrO_3 to atmospheric hydrated limestone in the water of hydration increases capture by about 18 percent.

It was noted earlier that chromium compounds are precluded as additives in practical applications for environmental and economic reasons. Sodium functions impressively as a promoter but may, in specific applications, adversely affect a boiler's slagging characteristics. An inexpensive promoter with minimal adverse effects was sought in further testing at EERC with attention being directed to iron. Physical mixing of iron compounds with all sorbents proved to be of no benefit. In preliminary testing, the addition

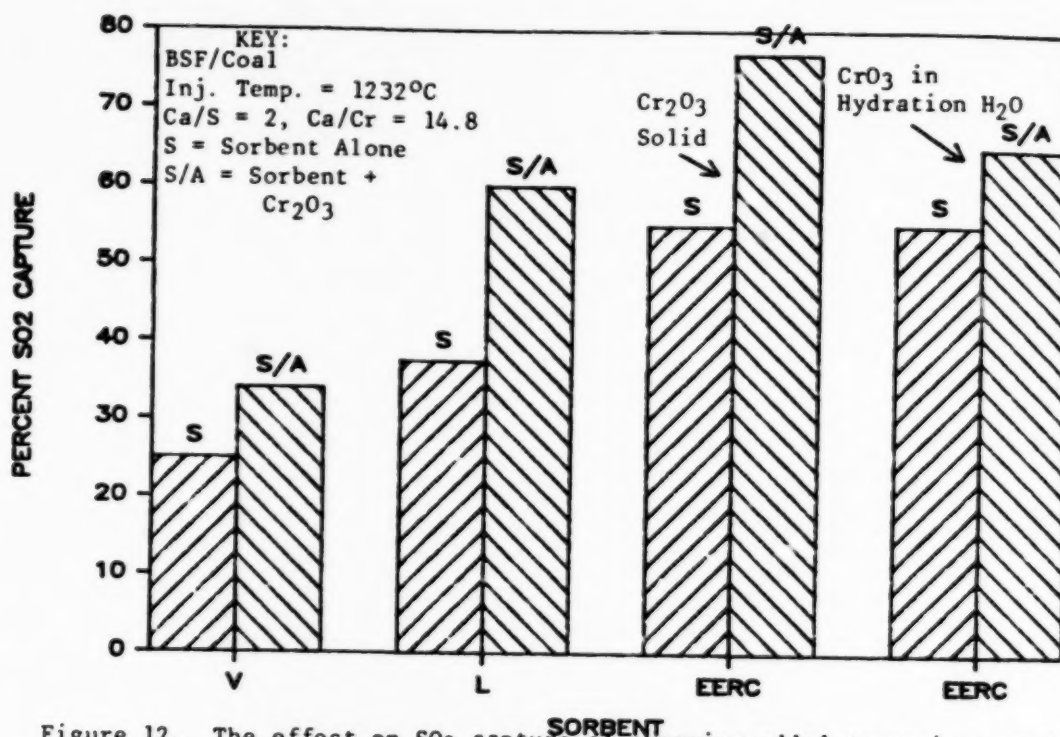


Figure 12. The effect on SO₂ capture of chromium added to various sorbents (V = limestone, L = atmospheric hydrated limestone, EERC = pressure hydrated limestone).

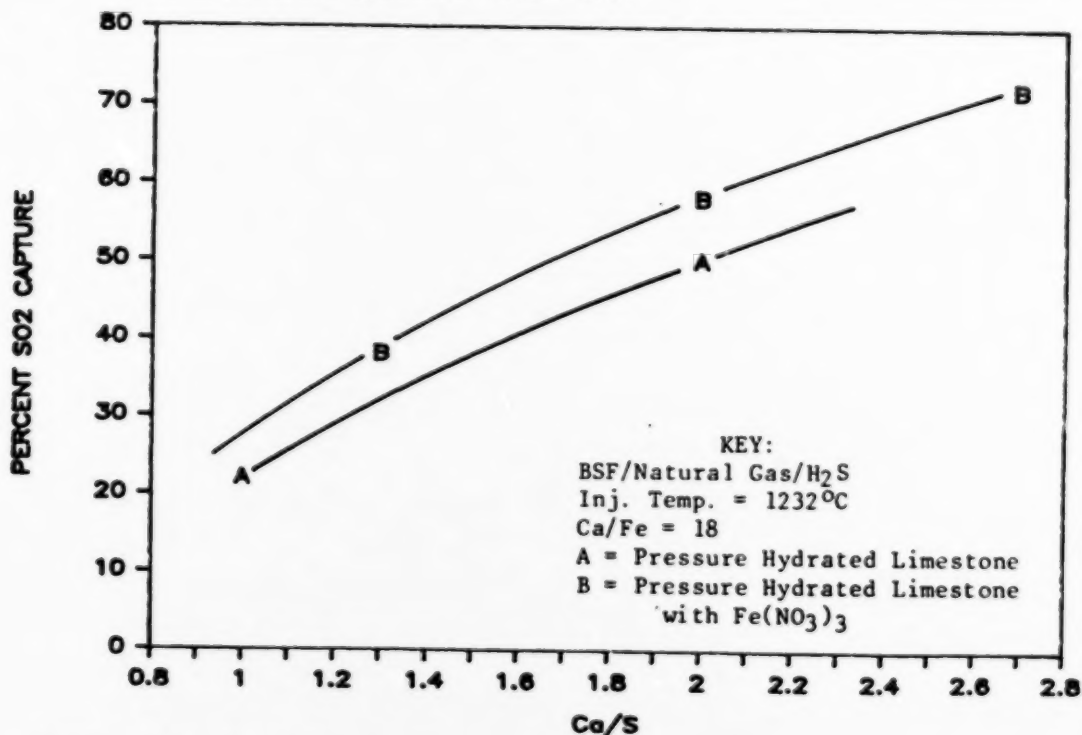


Figure 13. The effect on SO₂ capture by iron added to pressure hydrated limestone in the hydration water.

of $\text{Fe}(\text{NO}_3)_3$ to the water of hydration in pressure hydrated limestones, however, appeared to increase SO_2 capture by 20 percent. Figure 13 shows this effect.

CONCLUSIONS

It has been shown that the primary variable affecting sorbent reactivity at high temperature or at low temperature with water droplets is surface area. For the development of high surface area during furnace injection, some limestones appear to be superior to others and can be selected accordingly. Even more striking are the differences in surface area development and sulfur capture between classes of commercially available sorbents. Dolomitic sorbents generally outperform their calcitic counterparts, and hydrates are clearly preferable to carbonates on the basis of SO_2 capture. It has been shown further that sorbents can be modified in a number of ways to enhance their performance. Limestones can be precalcined to high surface areas and injected downstream from the burner to preserve their reactivity. Calcitic materials can be pressure hydrated to increase their reactivity over atmospheric hydrates, and hydration parameters can apparently be adjusted to increase reactivity even further. Finally, additives are available which promote SO_2 capture in the full range of calcium-based sor-

bents, and iron has been identified as an effective promoter with minimal adverse effects when added to the water of hydration for pressure hydrated materials.

REFERENCES

1. Nurick, W., Payne, R., Lee, J., Case, P., Chen, S., and Pershing, D., "Development of Criteria for Extension of Applicability of Low-Emission, High-Efficiency Coal Burners: Third Annual Report," EPA-600/7-81-171c (NTIS PB82-197153), October 1981.
2. Chen, S., Pershing, D., and Heap, M., "Bench-Scale Evaluation of Non-U.S. Coals for NO_x Formation Under Excess Air and Staged Combustion Conditions," EPA-600/7-83-025 (NTIS PB83-196014), April 1983.
3. Sedor, P., "Pilot Plant Study of Additive Injection for SO₂ Control," presented at the National Air Pollution Control Administration Dry Limestone Injection Process Symposium, Gilbertsville, KY, June 22-26, 1970.
4. Whitten, C. and Hagstrom, R., "Pilot Plant Moving Grate Furnace Study of Limestone-Dolomite for Control of Sulfur Oxide in Combustion Flue Gas (Final Report)," EPA report APTD 1264 (NTIS PB 184944), May 1969.

5. Gartrell, F., "Full Scale Desulfurization of Stack Gas by Dry Limestone Injection, Volume I," EPA-650/2-73-019a (NTIS PB 228447), August 1973.
6. Zallen, D., Gershman, R., Heap, M., and Nurick, W., "The Generalization of Low Emission Coal Burner Technology," In Proceedings of the Third Stationary Source Combustion Symposium, Volume II, EPA-600/7-79-050b (NTIS PB 292540), February 1979.
7. Case, P., Heap, M., Lee, J., McKinnon, C., Payne, R., and Pershing, D., "Use of Sorbents to Reduce SO₂ Emissions from Pulverized-Coal Flames Under Low-NO_x Conditions (Progress Report)," EPA-600/7-82-060 (NTIS PB83-131045), September 1982.
8. Payne, R., Case, P., Heap, M., Lee, J., McKinnon, C., Nelson, P., and Pershing, D., "Development of Criteria for Extension of Applicability of Low-Emission, High-Efficiency Coal Burners: Fourth Annual Report," EPA-600/7-84-087 (NTIS PB84-240654), August 1984.

9. Drehmel, D., Martin, G., Milliken, J., Abbott, J., "Low NO_x Combustion Systems with SO₂ Control Using Limestone," paper #83-38.7, APCA Annual Meeting, Atlanta, GA, June 1983.
10. Drehmel, D., Martin, G., Abbott, J., "Results from EPA's Development of Limestone Injection Into a Low NO_x Furnace," In Proceedings: Eighth Symposium on Flue Gas Desulfurization, New Orleans, LA, November 1983, Volume 1, EPA-600/9-84-017a (NTIS PB84-223031), July 1984.
11. Freund, H. "The Kinetics of Limestone/Dolomite with H₂S under Rich Combustion Conditions," Combustion Science and Technology, 26 (42): 83-88, 1981.
12. Harvey, R. D., "Petrographic and Mineralogical Characteristics of Carbonate Rocks Related to Sulfur Dioxide Sorption in Flue Gases," EPA report APTD-0920 (NTIS PB206487), July 1971.
13. Drehmel, D. C., "Test to Evaluate Reactivity of Boiler Calcined Limestone Used in Air Pollution Control," Bulletin of American Ceramic Society, 50 (8): 666-670, August 1971.

14. Kirchgessner, D., "Laboratory-Scale Production and Characterization of High Surface Area Sorbents," In Proceedings: First Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, Volume 1: Fundamental Research and Process Development, EPA-600/9-85-020a (NTIS PB85-232353), July 1985.
15. Newton, G., Harrison, D., Silcox, G., and Pershing, D., "Control of SO_x Emissions by In-Furnace Sorbent Injection: Carbonates vs. Hydrates," presented at AIChE Annual Meeting, Chicago, IL, November 1985.
16. Harrison, D., Newton, G., and Pershing, D., "Calcination of Calcium-Based Sorbents for Control of SO₂ Emissions from Coal Fired Boilers," presented at Western States Section/The Combustion Institute Fall Meeting, Davis, CA, October 1985.
17. Overmoe, B., Chen, S., Ho, L., Seeker, W., Heap, M., and Pershing, D., "Boiler Simulator Studies on Sorbent Utilization for SO₂ Control," In Proceedings: First Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, Volume 1: Fundamental Research and Process Development, EPA-600/9-85-020a (NTIS PB85-232353), July 1985.

18. Beittel, R., Gooch, J., Dismukes, E., and Muzio, L., "Studies of Sorbent Calcination and SO₂ Sorbent Reactions in a Pilot-Scale Furnace," In Proceedings: First Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, Volume 1: Fundamental Research and Process Development, EPA-600/9-85-020a (NTIS PB85-232353), July 1985.
19. Bortz, S. and Flament, P., "Recent IFRF Fundamental and Pilot Scale Studies on the Direct Sorbent Injection Process," In Proceedings: First Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, Volume 1: Fundamental Research and Process Development, EPA-600/9-85-020a (NTIS PB85-232353), July 1985.
20. Slaughter, D., Silcox, G., Lemieux, P., Newton, G., and Pershing, D., "Bench Scale Evaluation of Sulfur-Sorbent Reactions," In Proceedings: First Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, Volume 1: Fundamental Research and Process Development, EPA-600/9-85-020a (NTIS PB85-232353), July 1985.

21. Borgwardt, R., Bruce, K., and Blake, J., "EPA Experimental Studies of the Mechanisms of Sulfur Capture by Limestone," In Proceedings: First Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, Volume 1: Fundamental Research and Process Development, EPA-600/9-85-020a (NTIS PB85-232353), July 1985.